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Synthesis and properties of cationic surfactants with tuned hydrophylicity

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Abstract

A series of pyridinium-based cationic surfactants has been synthesized and their amphiphilic properties have been studied by conductivity and surface tension measurements. The modification of the substitution pattern on the pyridinium ring by hydrophobic moieties (methyl vs. hydrogen

and presence or not of condensed benzene ring) gave the opportunity to investigate structure-activity relationships. Characterization by conductivity and surface tension measurements shed light on the behavior at the air/water interface and in the micellar environment. In particular, the tendency to form ion pairs at very low concentration was evidenced for all the surfactants substituted on the ring, but not for the simple pyridinium ones. The formation of ion pairs affects both the conductivity and the surface tension plots, showing that a series of steps is involved during the adsorption to the air/water surface. An attempt was made to qualify the single steps in the adsorption at the surface layer. Those steps were attributed to different chemical species (free surfactant ions or ion pairs) and to different arrangements of the surfactant. This work also represents a contribution of investigation at very low surfactant concentrations and high surface tension values.

Keywords: cationic surfactants, pyridinium, surface tension, conductivity, amphiphilic properties, Gibbs paradox.

1. Introduction

Cationic surfactants have attracted the attention of chemists for a long time, due to their general simple synthesis and their broad application in several fields. Pyridinium surfactants [1], in particular, are important as ingredients of cosmetic products [2], and are also used as corrosion inhibitors [3], in emulsion polymerization [4] and textile processing [5]. Within biological applications, they show a good antimicrobial activity [6] and can be used as drugs [7], gene delivery agents [8] or in DNA extraction methods [9]. Quite recently, cationic pyridinium surfactants have found applications in the synthesis of TiO₂ nanoparticles [10], in ionic liquids synthesis [11] or as electrolytes for dye-sensitized solar cells [12].

The aim of the present work was the synthesis and the characterization of a series of cationic pyridinium and quinolinium surfactants. The investigation of their behaviour was performed by conductivity and surface tension measurements trying to evaluate the influence of the modification of the headgroup polarity on the aggregation properties. The obtained results can be helpful for their use in a wide range of applications.

2. Materials and Methods

2.1 Materials

All the chemicals were purchased from Sigma Aldrich, and were normally freshly distilled before use. The glassware used for synthesis was heated overnight in an oven at 150°C and assembled in the oven, then cooled under Ar flux before starting the reactions.

Melting points were taken on a hot plate equipped with a microscope and are uncorrected.

¹H-NMR (400 MHz) spectra were recorded on a Jeol EX400 NMR spectrometer in DMSO-d₆ using the DMSO signal as a reference. NMR signals are described by use of s for singlet, d for doublet, t for triplet, m for multiplet.

FT-IR spectra were recorded in KBr on a Shimadzu FT-IR Spectrometer.

UV spectra were recorded on a Shimadzu UV-1700 spectrometer. For the evaluation of the surfactants concentration after their purification, several solutions at different concentration were used as standards in order to build a regression plot.

ESI-MS spectra (positive ions) were recorded using a LCQ Deca XP plus spectrometer (Thermo), with electrospray interface and ion trap as mass analyzer. The flow injection effluent was delivered into the ion source using nitrogen as sheath and auxiliary gas.

TLC were performed on silica gel 60 F₂₅₄ or basic alumina plates using BAW (Butanol:Acetic Acid:Water 4:1:5, organic phase) as eluents.

2.2 General Procedures

The synthesis of ***N*-(*n*-Dodecyl)-4-methylpyridinium Bromide (2b)** and ***N*-(*n*-Dodecyl)-4-methylquinolinium Bromide (3b)** were already reported [6].

***N*-(*n*-Dodecyl)-4-methylquinolinium Iodide (3c):** 4 g of 4-methylquinoline (0.028 mol) and 10.7 g of iodododecane were introduced under nitrogen in a round bottom flask. Dry toluene was added and the reaction was stirred and warmed at 120°C for 6 hours. The resulting mixture was cooled to room temperature and washed repeatedly with diethyl ether to remove both iodododecane and toluene. The residue was dissolved in methyl ethyl ketone and evaporated under reduced pressure. The resulting viscous paste was warmed with water, giving a yellow solid that was filtered on a Hirsh funnel. The product was recrystallized in warm ethanol and cooled in a refrigerator, giving yellow-greenish crystals. Yield 80%, after crystallization 65%. M.p. 43-45°C. UV (ethanol) λ_{max} 221, 317 nm, $\log \epsilon = 4.10, 3.73$. ^1H NMR (DMSO- d_6): δ 0.84 (t, 3H, CH₃), 1.22 (broad, 18H, 9CH₂), 1.93 (m, 2H, CH₂CH₂N⁺C₁₀H₇), 3.00 (s, 3H, CH₃), 4.99 (t, 2H, CH₂N⁺C₁₀H₇), 8.05 (t, 1H, Ar-H), 8.07 (d, 1H, Ar-H), 8.26 (dt, 1H, Ar-H), 8.54 (dd, 1H, Ar-H), 8.59 (d, 1H, Ar-H), 9.40 (d, 1H, Ar-H). MS-ESI (+): 312 [M]⁺. Anal. Calcd. from C₂₂H₃₄IN: C, 60.13; H, 7.80; N, 3.19. Found: C, 60.16; H, 7.79; N, 3.20.

***N*-(*n*-Dodecyl)-4-methylquinolinium Chloride (3a):**

The strong basic ion exchanger was previously conditioned in sequence with water, 10% aqueous NaOH, 10% NaCl and washed thoroughly with water to remove any inorganic salt excess. Finally, the ion exchanger was filtered on a Buchner funnel and conditioned with methanol. The resin was put in a chromatographic column and was conditioned with 2-3 column volumes of methanol. The iodide salt (**3c**) was dissolved in methanol and was eluted through an ion exchange column. The effluent was recovered and the solvent was evaporated under reduced pressure. The final product was crystallized at least thrice from acetone, obtaining white crystals. Yield: 99%. M.p. 105-108°C. UV (ethanol) λ_{max} 243, 319 nm, $\log \epsilon = 3.82, 3.70$. ^1H NMR (DMSO- d_6): δ 0.84 (t, 3H, CH₃), 1.22 (broad, 18H, 9CH₂), 1.93 (m, 2H, CH₂CH₂N⁺C₁₀H₇), 3.00 (s, 3H, CH₃), 5.02 (t, 2H, CH₂N⁺C₁₀H₇), 8.05 (t, 1H, Ar-H), 8.08 (d, 1H, Ar-H), 8.26 (dt, 1H, Ar-H), 8.54 (dd, 1H, Ar-H), 8.60 (d, 1H, Ar-

H), 9.46 (d, 1H, Ar-H). MS-ESI (+): 312 [M]⁺. Anal. Calcd. from C₂₂H₃₄ClN: C, 75.94; H, 9.85; N, 4.03. Found: C, 75.96; H, 9.82; N, 4.03.

2.3 Conductivity measurements

Conductivity measurements were performed on a conductivity meter equipped with a conductivity cell having a cell constant of 0.943 cm⁻¹ as already reported [6]. The temperature was 25.0±0.1 °C and the standard deviation for conductivity was estimated around 2% as a maximum over three runs. The addition of concentrated surfactant solution by a titrator and the collection of the conductivity data were performed by using a computer controlled automated system, working with a program written in Quick Basic, available from the authors. Water of MilliQ quality (conductivity: 0.05 mS; surface tension: 72.8 mN/m at 20°C) was used for the measurements.

2.4 Surface Tension Measurements

The surface tension was measured by using a digital tensiometer. Measurements were made at 25±0.1°C using the Wilhelmy plate [13]. Sample temperature was controlled to 0.1°C by using a circulating water thermostatic bath. The instrument was calibrated against MilliQ water, equilibrated against atmospheric CO₂, each time measurements were done. Since cationic surfactants adsorb onto negatively charged glass surfaces, all glassware was thoroughly soaked with the solution to be measured; soaking solutions were discarded. Sets of measurements were taken at 15 min intervals until no significant change occurred, provided that stability was attained in one hours or less. Standard deviation of the surface tension measurements was less than 0.1 mN/m. The absence of a minimum in the surface tension vs. log concentration plot in the post-cmc region showed that there was very little or no surface active impurity present in the final products.

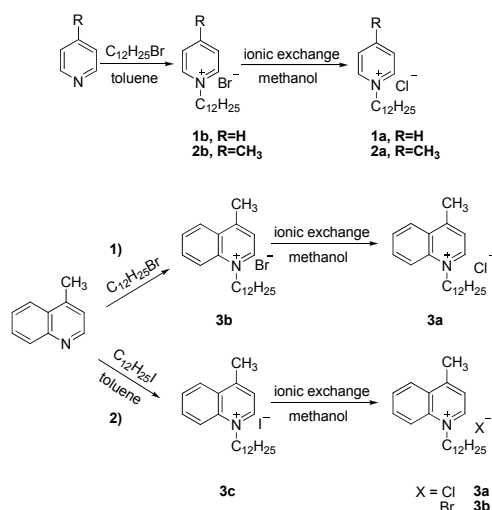
Before tension measurements, all the surfactants have been purified. Surfactant solution purification was carried out on RP18 cartridges modifying a literature procedure [14, 15]. Instead of using a syringe directly attached to the RP18 cartridge, our method is similar to a flash

chromatography, with a glass column directly connected at the bottom of the cartridge. RP-18 columns were wetted with 2 ml of methanol and then three washings with 5 ml of MilliQ water were performed. Then, an aqueous solution of the surfactant (about 50 ml), at a concentration 5 times the expected cmc, was passed through the column in order to absorb hydrophobic impurities. This step was repeated 5 times. The concentration of surfactants in the effluent from the column was determined by UV absorbance. From this stock solution, dilutions were prepared (25 ml). Every diluted surfactant solution was further purified in the same way, by flowing it through the same RP18 column (10 times, nearly 10-15 minutes total time). In this way, preferential adsorption of more hydrophobic impurities occurs. After checking the correct surfactant concentration, the surface tension of solutions was measured. The method used by Lunkenheimer [16] has the advantage of being automatic, but it is time consuming and the preparation of the PC controlled machine is not trivial. Even if our procedure cannot guarantee for a certain result (sometimes even the Lunkenheimer method fails), a test can be done to check for the surface tension stability to be attained in one hour, for both the mother solution and at least one dilution.

3. Results and Discussion

3.1 Synthesis

Surfactants **1b** and **2b** were prepared by refluxing pyridine or 4-methylpyridine, respectively, with dodecyl bromide in dry toluene following a modification of a standard procedure [6]. The use of toluene as solvent, instead of a big excess of alkyl halides [15], gave better yields, making the purification steps easier. Compounds **1a-2a** were thus obtained by ionic exchange as described in Scheme 1.



Scheme 1: Compounds prepared and characterized in the present work.

In a previous work we reported the synthesis of **3b** following the standard procedure using 4-methylquinoline and dodecyl bromide as the solvent [6] (Scheme 1, pathway 1). While this reaction is simple to manage and the product is easily obtained, its purification and the subsequent ionic exchange to obtain **3a** were difficult (coloured impurities were difficult to remove, even by several crystallizations), thus reducing considerably the final yield. To overcome these problems, highly pure compound **3c** was prepared by reacting the 4-methylquinoline with dodecyl iodide in dry toluene at reflux (Scheme 1, pathway 2). At the end of the reaction, a phase separation occurred on cooling to room temperature, giving a red oily phase as product. This oil, washed with ethyl ether to remove the residual reactants, gave a fine yellow powder after its treatment with water. This powder was finally crystallized three times from absolute ethanol. Compounds **3a-b** were thus prepared by ionic exchange from compound **3c**. The ionic exchange step was performed by using methanol as the solvent instead of water in order to avoid product solubility problems and limiting the formation of coloured impurities. The resulting solution of the product was simply evaporated obtaining off-white products which were crystallized three times from acetone. These compounds were then used for the amphiphilic characterization after the purification of their solutions in water by repeated

passages through a RP-18 column to remove any traces of more surface active impurities (see the experimental section).

3.2 Cmc determination

The amphiphilic behaviour of the synthesised surfactants was carried out by surface tension (Fig. 1) and conductivity measurements (Fig. 2) and results are reported in Table 1.

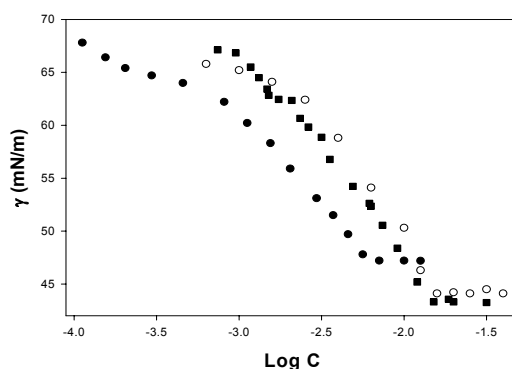


Figure 1. Surface tension vs. LogC plots for 1-dodecylpyridinium chloride **1a** (○), 1-dodecyl-4-methylpyridinium chloride **2a** (■); 1-dodecyl-4-methylquinolinium chloride **3a** (●).

Table 1. Critical Micellar Concentrations for the studied surfactants evaluated by surface tension and conductivity.

Compound	CMC ^a (mM)	β ^a %	Discontinuity before cmc ^a (mM)	CMC ^b (mM)	β ^b %	Discontinuity before cmc ^b (mM)	CMC ^c (mM)	Discontinuity before cmc ^c (mM)
1a	17.0	60	-	16.5	59	-	16.2	
1b	11.3	73	-	11.3	73	-	11.5	
2a	15.1	56	0.25 (6)	15.7	63	0.24 (7)	14.2	1.51
2b	8.1	77	0.28 (20)	9.1	77	0.26 (19)	9.15	0.32
3a	7.39	46	0.26 (21)	7.21	46	0.23 (21)	7.76	0.52
3b	4.9	68	0.12 (9) 0.27 (26)	4.7	70	0.095 (17) 0.27 (31)	4.3	0.019 0.1

(a): from conductivity, classical method; (b): from conductivity, nonlinear fit; (c): from surface tension. Values in parenthesis are β values recorded at the reported discontinuities.

Beside the evaluation of the cmc, several parameters can be obtained from surface tension measurements by using the Gibbs adsorption equation, in which N is the Avogadro number and n (the number of ionic species whose concentration at the interface varies with the surfactant concentration in solution) is taken as 2.

$$\Gamma_{\max} = -\frac{1}{2.303nRT} \left(\frac{\partial \gamma}{\partial \log C} \right)_T \quad (1)$$

$$A_{\min} = \frac{10^{16}}{N\Gamma_{\max}} \quad (2)$$

They are reported in Table 2: i) γ_{cmc} , the surface tension at the cmc (which measures the effectiveness of surface tension reduction), ii) the maximum surface excess concentration Γ_{\max} [mol \AA^{-2}] (equation 1), iii) the minimum area per molecule at the interface A_{\min} [\AA^2] (equation 2), iv) the C_{20} (or $\text{p}C_{20}$), i.e. the efficiency in surface tension reduction, i.e. the molar surfactant concentration required to reduce the surface tension of the solvent by 20 mN/m and vi) the cmc/C_{20} ratio (which estimates the tendency of the surfactant to form micelles relative to the tendency to adsorb at the air/water interface).

The conventional Gibbs adsorption model has been recently questioned [17] on the basis of the results from measurements of water evaporation rate [18,19], surface potential [17,20], Brewster Angle Microscopy (BAM) [17,18] and fluorescence [21], suggesting that the surface excess of surfactant does not locate at the air-water interface but below it, structured, probably, as a bilayer. Even if this new model could be very intriguing, it lacks at the present moment quantitative treatment of surface tension data. Until now the treatment of surface tension data by the Gibbs isotherm has the advantage to provide very useful parameters in order to compare, even if in a conventional way, the behaviour of the different surfactants. The reported numbers have to be considered mean values, referred to a surface layer not ordered, constituted by surfactant molecules in very fast equilibrium with the bulk and structured very differently from an insoluble monolayer protecting the surface.

Table 2. Surface tension characterization of surfactants **1-3**.

Compound	CMC (mM)	γ_{cmc} (mN/m)	Γ_{\max} (mol/ \AA) ($\cdot 10^{-10}$)	A_{\min} (\AA^2)	C_{20} (mM)	CMC/ C_{20}
1a	16.2	44.2	2.7	62	8.13	1.80
1b ^[15]	11.5	39.1	3.3	50	4.68	2.50
2a	14.2	43.4	2.23	74	6.03	2.34
	1.51	62.5	1.57	106		

2b ^[6]	9.15	40.0	2.43	68	3.16	2.79
	0.32	64.5	1.67	100		
3a	7.76	47.2	1.8	92	3.02	2.52
	0.52	65.4	0.81	285		
3b ^[6]	4.3	42.3	1.96	85	1.48	2.88
	0.1	65.4	0.61	271		
	0.019	68.5	0.31	541		

As far as the conductivity measurements are concerned, the cmc values were obtained from specific conductivity κ vs. surfactant concentration by the intersection of the lines fitted in the diluted and concentrated regions before and after the cmc. Fig. 2 shows the variation of the specific conductivity κ with the concentration C for compound **2a** as an example. Besides, the evaluation of the degree of counterion dissociation α can be carried out from the ratio of the slopes obtained above and below the cmc while the degree of counterion binding can be obtained by using $\beta = 1 - \alpha$.

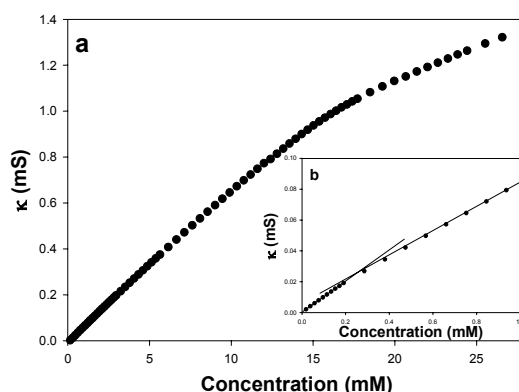


Figure 2. Conductivity plots for 1-dodecyl-4-methylpyridinium chloride (**2a**): a) specific conductivity κ vs. C plot; b) low concentration range of the plot as in a. A discontinuity in this range is revealed.

It should be stressed that a more reliable way to obtain the value of β is connected with the Corrin-Harkins plot reporting $\log \text{CMC}$ vs $\log(\text{CMC} + \text{concentration of added salt})$ [22]. However, since most of the previous literature was essentially based on β values obtained from the classical method, we prefer to report here values obtained according to the two methods shown above to permit an adequate comparison.

Since for some surfactants the shape of the plots is smooth and the lines are quite difficult to be precisely defined, we also used a different approach in the conductivity data analysis based on a non linear fit introduced by Carpena et al. [23] which was successfully applied to our conductivity data on gemini ammonium [24] and gemini pyridinium surfactants [25, 26].

The data were fitted by the function reported in equation 3, which represents the integral function of a sigmoid:

$$F(x) = F(0) + A_1 x + \Delta x (A_2 - A_1) \ln \left(\frac{1 + e^{(x-x_0)/\Delta x}}{1 + e^{-x_0/\Delta x}} \right) \quad (3)$$

In this equation the transition from two linear regimes at low and high concentration is described. The parameters have the following meaning: $F(0)$ is the initial conductivity of water, A_1 and A_2 are the limiting slopes for low and high concentration respectively, x_0 is the central point of the transition, i.e. the cmc and Δx is the amplitude of the transition region between the premicellar and the postmicellar regions. The α value can be deduced from the ratio A_2/A_1 . Cmc values for compounds **1-3a** and **1-3b** are reported in Table 1 as obtained with both the data analysis methods.

A very good agreement between the cmc values found by conductivity and surface tension measurements is obtained. (Table 1). The cmc of surfactants with bromide counterion (**1-3b**) is lower than the cmc found for compounds with chloride counterion (**1-3a**) while the counterion binding β follows an opposite behaviour. The difference in cmc values is to be ascribed to the greater electrostatic attraction of the bromide series (**b**) compared to the chloride series (**a**) because of the smaller degree of hydration of the bromide ion [15]. This makes the hydrated chloride ion bigger than the bromide and less bound to the micelles, thus giving higher cmcs than corresponding bromide surfactants. If we look at the cmc trend for compounds **1-3** having the same counterion it is evident that the cmc of these surfactants decreases when a methyl group is inserted in position 4 (4-picolinium vs. 4-pyridinium) or a benzene is condensed to pyridine ring (quinolinium vs. pyridinium), in agreement with the higher hydrophobicity of the whole molecule and in agreement

with a previous work [27] where the authors showed that the presence of a 4-methyl group favours the aggregation process, leading to the formation of micelles.

The cmc decreases by increasing the hydrophobicity which makes the surfactants more surface active. This could be due to the higher crowding of the headgroup since the packing of headgroups at the air/water and micellar surface is a function of their dimension and ability to interact with water. In the case of chlorides surfactants series (**a**), the counterions bind to the micelle a bit less firmly when the headgroup is modified with methyl groups and the order seems to be related to both the headgroup dimensions and its ability to delocalize the positive charge. This means that when the dimension of the headgroup grows, the repulsion among the headgroups reduces, thus requiring less counterion bound to the micelle to obtain a stable aggregate. As far as headgroups dimensions are concerned, a bigger headgroup gives less packed layers at the air/water surface and the surface water hydrogen bond network is less disturbed by the surfactant packing. This would account for a lower surface tension reduction. Moreover, when the headgroup is big, for the compounds under investigation, the positive charge is more dispersed and the headgroup keeps the counterion less firmly bound to itself (see Table 1), resulting in a less packed layer at the air/water surface. The headgroup dimension increase gives a higher minimum area per molecule (A_{\min}) at the cmc, thus confirming that the headgroup modifications give a less packed layer at the surface. The presence of a methyl group on the pyridinium ring increases the minimum area per molecule at the interface of about 12-18 Å² (compare compounds **1a-b** to **2a-b**) while the addition of a fused phenyl ring increases the minimum area of 17-18 Å² (compare compounds **2a-b** to **3a-b**). In principle, a larger increase should be expected due to the larger volume increase for compounds **3a-b** over **2a-2b**. This should indicate that the pyridinium and quinolinium ring should not stay flat onto the surface but, instead, tilted of a certain angle. Probably the arrangement at the surface of the 4-methylpyridinium and of the 4-methylquinolinium rings is different from each other, with the pyridinium ring more tilted from the perpendicular arrangement than the quinolinium one, in order to leave the methyl group to escape better from the contact with water. The quinolinium ring may adopt an arrangement

more similar to the perpendicular one, to keep away the second aromatic ring, i.e. the bigger hydrophobic component of the headgroup, from contact with water.

3.3 Discontinuity at low concentration

Surfactants **2a-3a** and **2b-3b**, for which the headgroup was modified by hydrophobic components (methyl and condensed benzene), show the occurrence of a discontinuity in the low concentration range detected both by conductivity and surface tension measurements (see Fig. 1 for compounds **2a-3a** and Fig. 2 - panel b for compound **2a**). The concentrations at which these discontinuities occur are reported in Table 1. As an example, the occurrence of the discontinuity for compound **2a** was detected well below the cmc, near about 0.25 mM (see Fig. 2). At this discontinuity point, β value, ranging from 6 to 26%, is too low to account for micelle formation while it can be taken as an evidence for the occurrence of ion pairs or premicellar aggregates.

Conductivity data were also studied by means of the molar conductivity Λ ($= \kappa - \kappa_0$)/C vs. $C^{0.5}$ plots (where κ_0 is the specific conductivity of water) in order to check the ion pairs or premicellar aggregates formation.

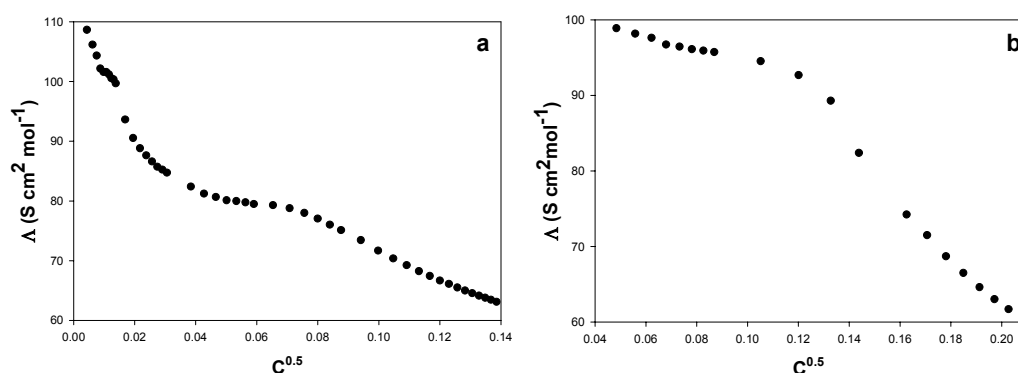


Figure 3. a) molar conductivity vs. $C^{0.5}$ plot for 1-dodecyl-4-methylpyridinium chloride (**2a**); b) molar conductivity vs. $C^{0.5}$ plot for 1-dodecylpyridinium chloride (**1a**).

The plot of Λ vs. $C^{0.5}$ (Fig. 3a for **2a**) shows that, for compounds which present a discontinuity in the specific conductivity κ vs. C plots, an asymptotical behaviour is evidenced at very low

concentration, while for compounds behaving regularly as **1a**, the asymptotic behaviour is not detected. This was taken as a symptom of the occurrence of ion pairs in solution. As already stated by Zana [28], the κ vs. C and the Λ vs. $C^{0.5}$ plots should be curved toward the concentration axes for ion pairs formation at relatively low concentration, that is exactly what we found (Fig. 3a). The insertion of a CH_3 group or condensed benzene was not large enough to promote premicellar aggregation for which a maximum in the Λ vs. $C^{0.5}$ plot should be found [28].

This was shown by Zana [28] in a study on gemini ammonium surfactants. In general this behaviour was recently found mostly for gemini surfactants, since they behave like more hydrophobic compounds [6, 25, 29]. Besides, studies on the formation of ion pairs in water and alcohols showed that the ion pairs have high tendency to form when the whole molecule hydrophobicity is growing [30, 31], i.e. the alkyl chain is lengthened. In this case, the hydrophobic moiety is added onto the headgroup, but it clearly contributes to the whole molecular hydrophobicity. For single chain N-dodecylpyridinium surfactants of this series, both chlorides (**a**) and bromides (**b**), a larger increase of the hydrophobicity is required to observe premicellar aggregation. This was found to occur for gemini ammonium surfactants [28], gemini pyridinium surfactants [26] and glucocationic surfactants [29].

Interestingly, the discontinuities found with surface tension at low concentration are in agreement with those evidenced by conductivity, taking into account that the two techniques are monitoring different molecular events (ion pairs formation for conductivity and ion pairs adsorption at the interface for surface tension) and that measurement errors are higher at low concentration. By increasing surfactant concentration, the ion pairs formation occurs and their concentration in solution increases [28]. In our interpretation, starting from very diluted solutions, only the simple surfactant ions are progressively adsorbed on the surface. As a second step, the ion pairs are adsorbed preferentially at the air/water surface since, by their nature they should behave as more hydrophobic species. The ion pairs probably adsorb, in about a flat arrangement at the surface until they saturate it, giving a peculiarity in the surface tension vs. $\log C$ plot that, in particular for

compounds **3a-b**, can show the occurrence of a short plateau at high surface tension values. In a third step their arrangement at the surface changes, and some hydrophobic part of the molecule, probably the chain, is removed from the water contact and raises in the air. At this step, the chains probably start to interact among them, due to dispersion forces. This gives more space at the surface, which can start to accumulate more surfactant molecules again. From this point on, a regular behaviour is observed, with surface tension decreasing until the cmc and the formation of a plateau indicating the complete air/water layer saturation. The minimum areas for those peculiarities are greater than those measured at the cmc and support this interpretation. From the surface tension plots, it seems that the higher the whole molecular hydrophobic character, the more evident the small plateau at high surface tension values.

3.4 Surface tension measurements at ionic strength 0.1 M

For compounds **1a-3a**, the surface tension was also measured at the ionic strength of 0.1 M, to see if and how the behaviour is affected by the added electrolyte. All surface properties results are reported in Table 3 and in Fig. 4 the surface tension vs. logC plot for compounds **2a** and **3a** are compared.

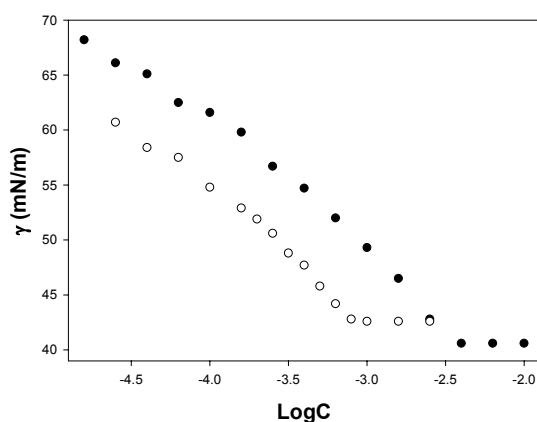


Figure 4. Surface tension vs. LogC plots for 1-dodecyl-4-methylpyridinium chloride **2a** (●) and 1-dodecyl-4-methylquinolinium chloride **3a** (○) at 25°C at ionic strength I = 0.1 M (KCl).

Table 3. Surface tension characterisation of surfactants **1a-3a** at 25°C, I = 0.1 M (KCl)

Compound	CMC	γ_{cmc}	Γ_{max}	A_{min}	pC_{20}	C_{20}	CMC/ C_{20}
	(mM)	(mN/m)	(mol/Å ²) ($\cdot 10^{-10}$)	(Å ²)		(mM)	
1a	1.91	30.0	3.94	42	3.37	0.428	4.46
2a	2.87	40.6	2.79	59	3.19	0.644	4.45
3a	0.814	42.6	2.7	61	3.70	0.198	4.11

By comparing the graphs in the presence and in the absence of added salts it is evident that, if any, the discontinuity at low concentration is more difficult to be detected, and only a slight, possible, peculiarity can be seen. The occurrence of this peculiarity was found to be in the same range of surface tension as for surfactants studied in pure water. We can try to explain those results by thinking that at high ionic strength the surfactants are behaving as not completely dissociated and the adsorption is, in fact, due only to ion pairs in the whole concentration range. However, the conditions of the adsorption are changed, in particular the ionic strength does not change with the surfactants concentration, and probably this makes it more difficult to detect a neat point at which the chains are removed from water contact. The cmc was found to reduce sensibly upon the addition of salt, according with general findings [15]. Also, the C_{20} value is reduced, due to enhanced tendency to the adsorption that is higher than the tendency to micellize (see that increase in CMC/ C_{20}) in those conditions. The surface activity is increased both from the efficiency (see C_{20}) and the effectiveness (surface tension reduction, γ_{cmc}) point of view. The minimum area per molecule increases as the headgroup size increases, while the absolute values are reduced from those obtained in pure water. The difference in A_{min} values among the compounds **1a-3a** are small and this can be interpreted with a better packing of the headgroups at the air/water interface, due to the reduced coulombic repulsion among headgroups at the ionic strength of 0.1 M. This means that the headgroups probably arrange at the surface in a more perpendicular way than that shown in pure water.

3.5 Gibbs paradox

The last portion of the surface tension decrease normally assumes a strictly linear shape, which is normally known as the “*Gibbs paradox*”, which was related by Lunkenheimer to the presence of very small quantity of hydrophobic impurities [16]. This behaviour is quite strange since the surface tension has to decrease due to the accumulation of surfactant molecules and it is evident that a certain degree of curvature towards the logC axis has to be found.

All the investigated surfactant solutions have been highly purified as described in the experimental section following a method which is a slight modification of that proposed originally by Rosen et al. [14, 15]. It is evident that, in our plots, there is a decrease with a slight but perceptible curvature towards the logC axis, which is a proof of the overcome of the Gibbs paradox. According to several authors [32-34] the surface tension decreasing portion of the curve can be fitted by a polynomial curve that well reproduces the trend and estimates the minimum area per molecule with good confidence. From this, the derivate at each experimental point can be obtained. Table 4 reports the percentage of occupied surface for compound **1** as an example.

Table 4. Surface adsorption parameters for 1-dodecylpyridinium chloride (**1a**).

Log C	γ (mN/M)	Γ (mol/Å ²) (*10 ¹⁰)	Area (Å ²)	Surface coverage ^a (%)
-1.8	44.1	2.6370	62.6	97.7
-1.9	47.1	2.4822	66.9	91.9
-2.0	50.3	2.3181	71.6	85.9
-2.2	54.7	1.9746	84.1	73.1
-2.4	58.5	1.6310	101.8	60.4
-2.6	62.5	1.3080	126.9	48.4
-3.0	67.0	0.77550	214.1	28.7
-3.5	70.0	0.35448	468.4	13.1

a) calculated on the basis of the final surface excess at the cmc: $2.7 \cdot 10^{-10}$ mol Å²

It is evident that when the surface tension is about 62 mN/m, the surface coverage is about at 50%. The problem with surface tension measurements is that the surface tension starts decreasing

when a substantial number of the surface hydrogen bonds are broken, i.e. when the surface is covered, in general, for more than 50%. After this value of surface tension the slope of the curve increases substantially, i.e. the surface tension decreases more rapidly, giving more chances to obtain a better estimate for the surface excess and the minimum area per molecule. We could have some general confidence in using this approach since we could notice from the experimental points that the decrease of surface tension is giving a slight curvature of the decreasing surface tension portion of the plot until the cmc is attained (see Fig. 1). This was taken as an evidence of well behaving solutions, i.e. of solutions that can be considered nearly free from more hydrophobic impurities. It is noteworthy that in general the peculiarity shown at low concentration is found at about 62-65 mN/m and this would make very difficult to detect this behaviour. This should be the result of two independent facts. First, the ion pairs, when formed, start to transfer to the surface and, second, this surface tension range is attained when the surface coverage is about at 50%. When enough ion pairs reach the surface, i.e. when the surfactant is efficiently adsorbed (as a consequence of a highly hydrophobic whole structure), they can saturate the air/water layer, having a nearly flat arrangement on the surface. When the surface tension starts to decrease again, the removal of alkyl chain from the surface occurs, making the surface partially free and able to accumulate again more surfactant molecules. Lunkenheimer et al. [16] stressed the urge for performing measurements at very low concentration and high surface tension values to enhance the knowledge of the mechanisms underlying the early stages of the adsorption. Normally, however, surface tension measurements are used to detect the cmc and the low concentration range is often not investigated.

4. Conclusions

In this paper cationic surfactants having different hydrophobic moieties on the headgroup were prepared and their properties were measured by conductivity and surface tension measurements. The results show that the modification of the pyridinium ring by hydrophobic moieties (methyl and condensed benzene) enhances the tendency to form ion pairs in solution and that this has an effect

on the conductivity vs. C and surface tension vs. $\log C$ plots where significant discontinuities are shown. Besides, the discontinuities in the surface tension plots evidence that a transition between different arrangement of surfactants at the surface is occurring, when the surface coverage is about at 50%, probably due to the removal of the alkyl chain from the water contact or the rising of the pyridinium ring from a flat position on the surface to a near perpendicular arrangement.

Moreover, we proposed a purification method which can overcome the problem of the Gibbs paradox, giving curves having the “correct” shape and curvature and, in principle, can work for other surfactants. Actually, before surface tension measurements, all the studied surfactants have been purified by a simple and fast method (which is a slight modification of that proposed originally by Rosen [15]) which can work, at least in this case, as well as the Lunkenheimer one [34]. It should be stressed that even the Lunkenheimer method, while being a high performing one, can fail for some surfactants. However, the limit, for both methods, can be found in the hydrophobic difference among the surfactants and their impurities. When this difference is sufficiently high, the impurities can be efficiently separated. Most of times this hydrophobic difference is related to the difference in structure among surfactants and impurities.

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Figures captions

Scheme 1: Compounds prepared and characterized in the present work.

Figure 1. Surface tension vs. LogC plots for 1-dodecylpyridinium chloride **1a** (○), 1-dodecyl-4-methylpyridinium chloride **2a** (■); 1-dodecyl-4-methylquinolinium chloride **3a** (●).

Figure 2. Conductivity plots for 1-dodecyl-4-methylpyridinium chloride (**2a**): a) specific conductivity κ vs. C plot; b) low concentration range of the plot as in a. A discontinuity in this range is revealed.

Figure 3. a) molar conductivity vs. $C^{0.5}$ plot for 1-dodecyl-4-methylpyridinium chloride (**2a**); b) molar conductivity vs. $C^{0.5}$ plot for 1-dodecylpyridinium chloride (**1a**).

Figure 4. Surface tension vs. LogC plots for 1-dodecyl-4-methylpyridinium chloride **2a** (●) and 1-dodecyl-4-methylquinolinium chloride **3a** (○) at 25°C at ionic strength $I = 0.1$ M (KCl).

Table 1. Critical Micellar Concentrations for the studied surfactants evaluated by surface tension and conductivity.

Table 2. Surface tension characterization of surfactants **1-3**.

Table 3. Surface tension characterisation of surfactants **1a-3a** at 25°C, $I = 0.1$ M (KCl)

Table 4. Surface adsorption parameters for 1-dodecylpyridinium chloride (**1a**).